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(54) **OXIDE ETCH SELECTIVITY  
ENHANCEMENT**

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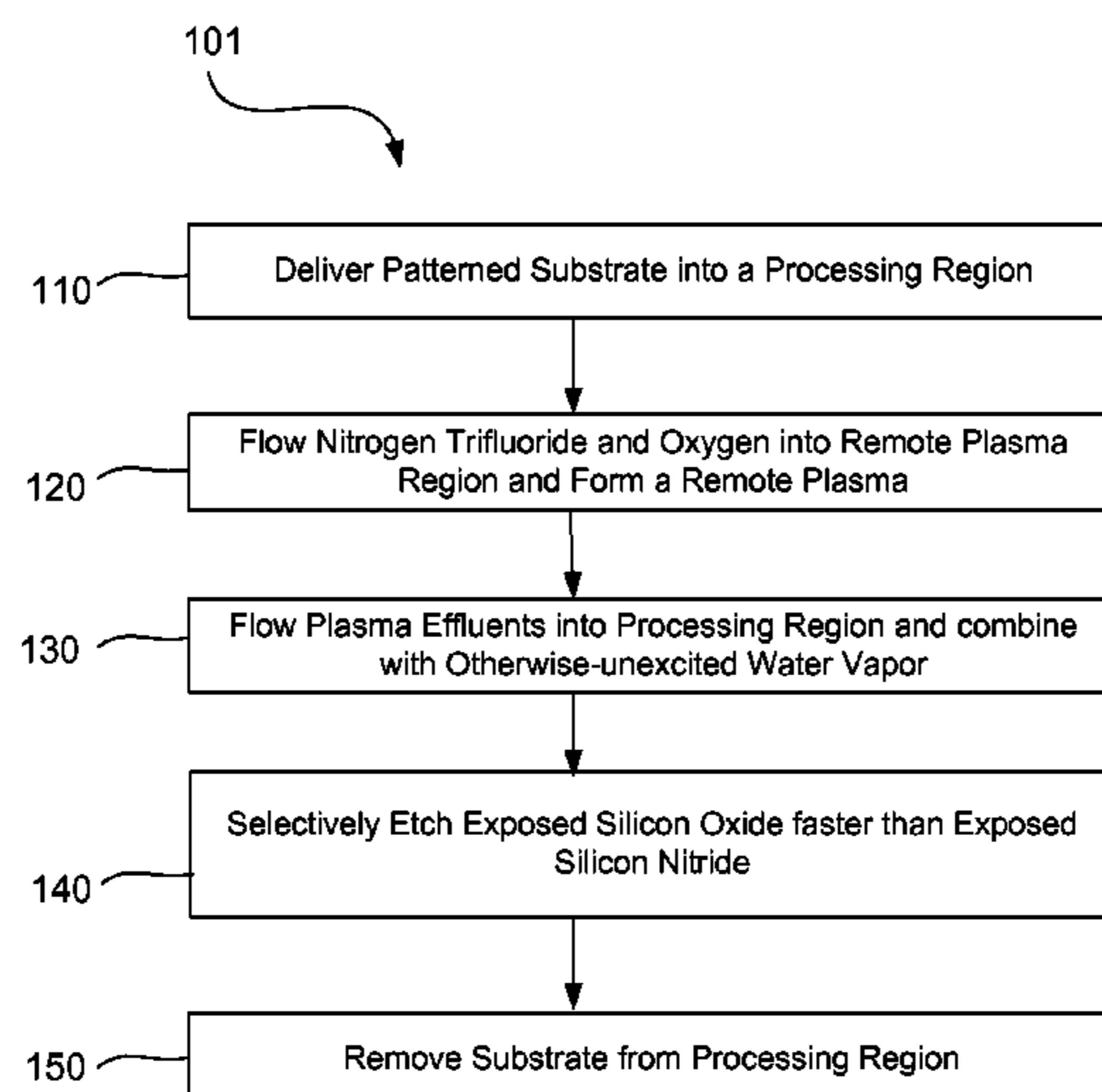
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(57) **ABSTRACT**

A method of etching exposed silicon oxide on patterned heterogeneous structures is described and includes a gas phase etch using plasma effluents formed in a remote plasma. The remote plasma excites a fluorine-containing precursor in combination with an oxygen-containing precursor. Plasma effluents within the remote plasma are flowed into a substrate processing region where the plasma effluents combine with water vapor or an alcohol. The combination react with the patterned heterogeneous structures to remove an exposed silicon oxide portion faster than an exposed silicon nitride portion. The inclusion of the oxygen-containing precursor may suppress the silicon nitride etch rate and result in unprecedented silicon oxide etch selectivity.

**12 Claims, 6 Drawing Sheets**



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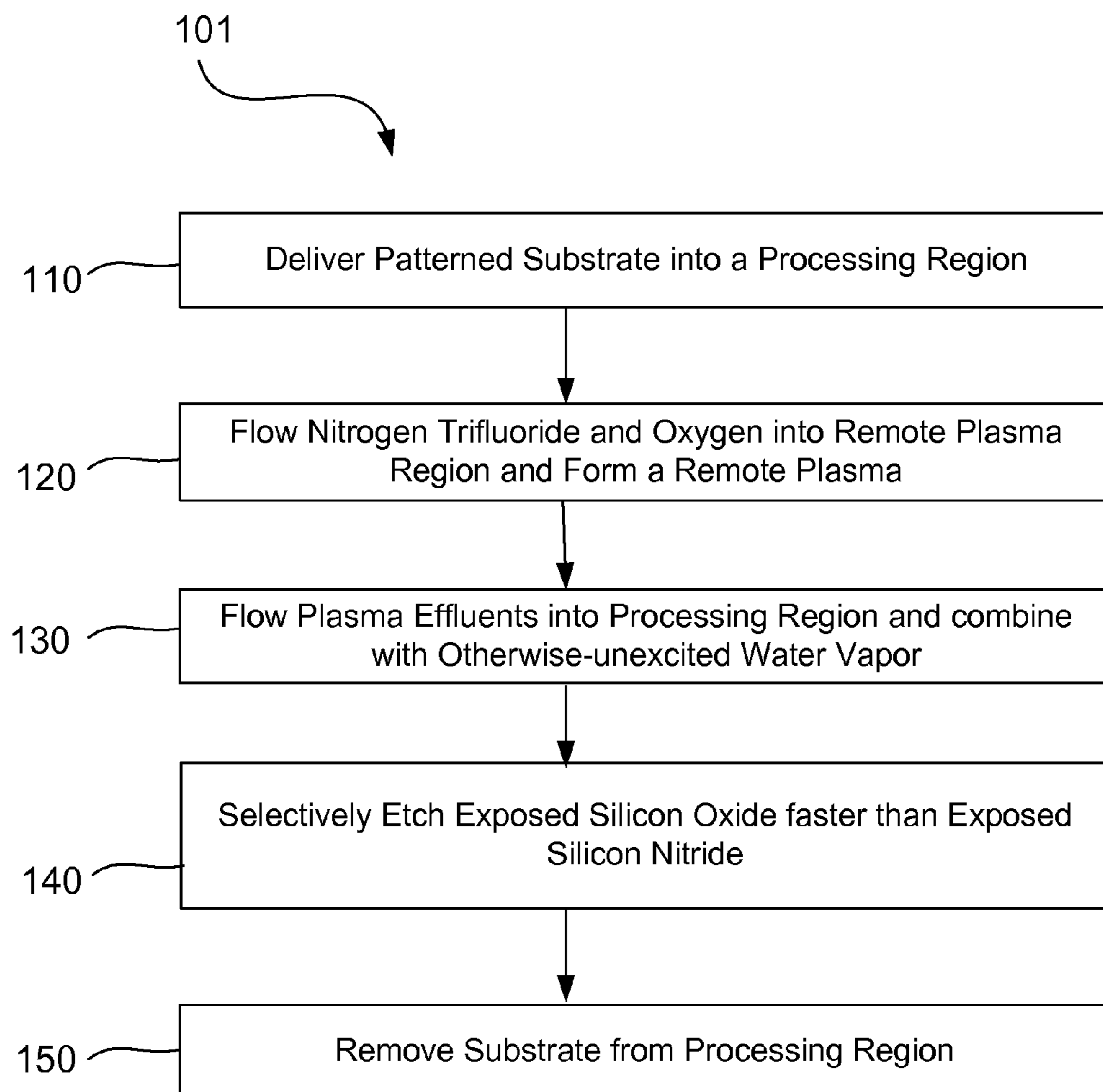


FIG. 1



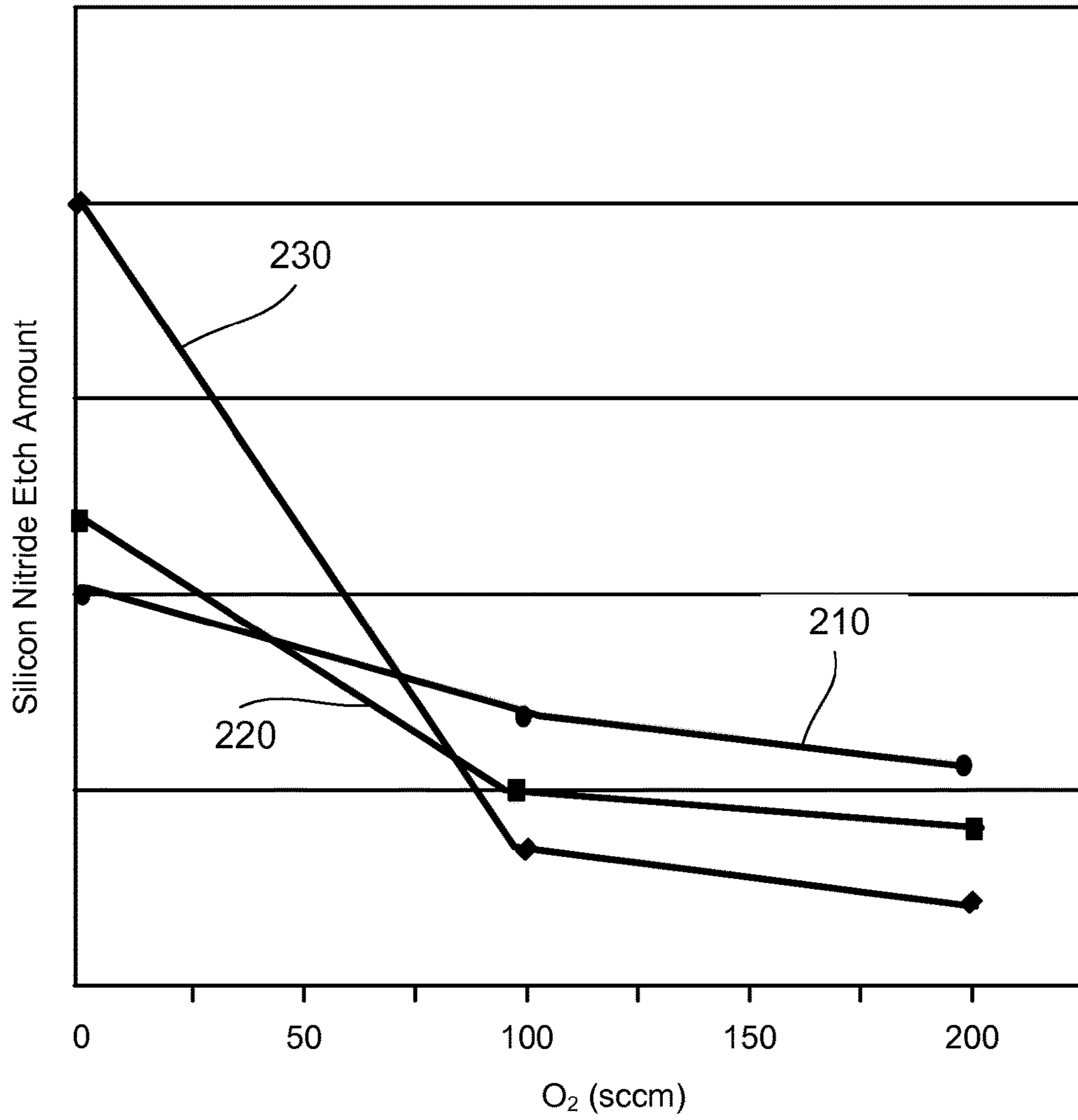
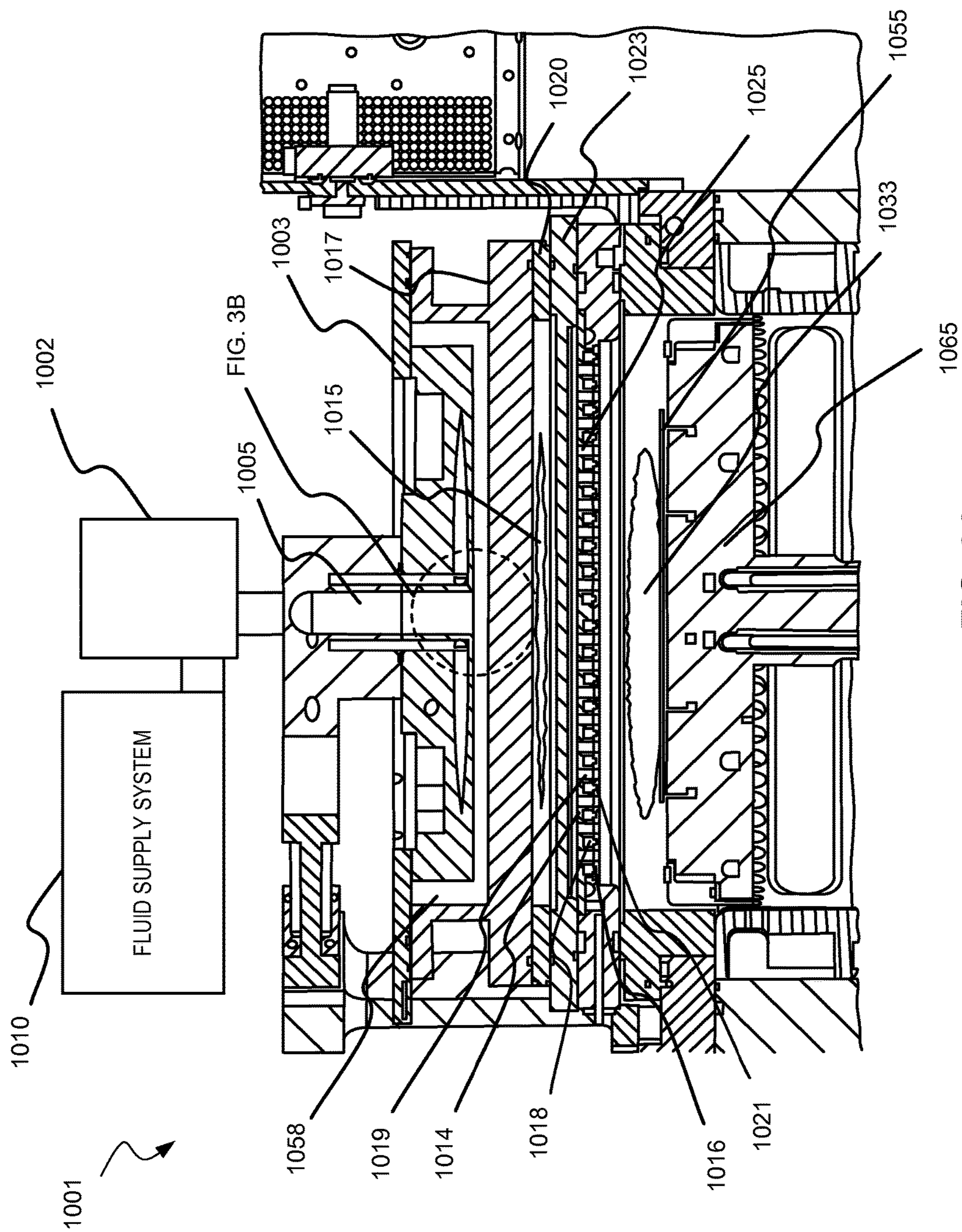


FIG. 2







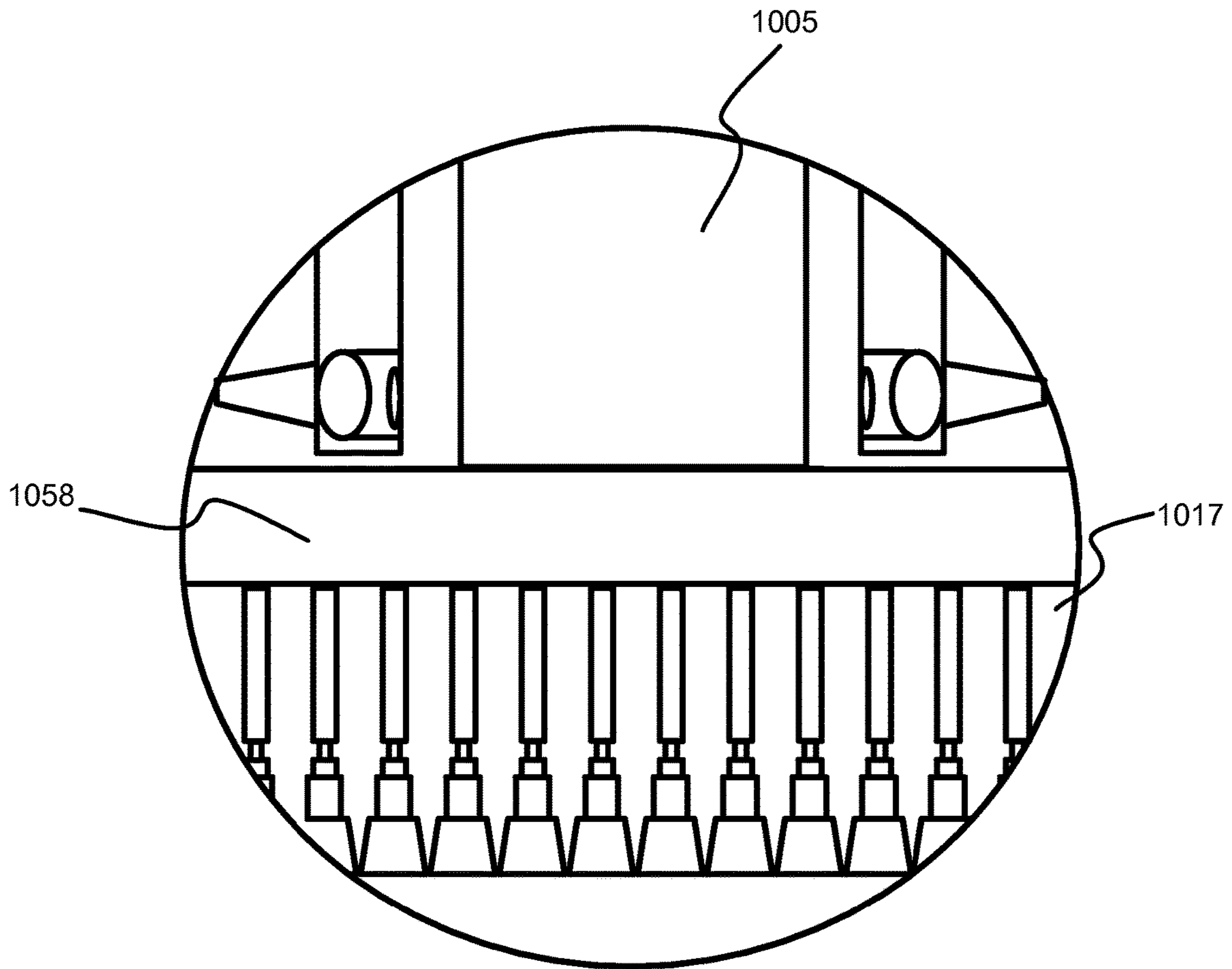


FIG. 3B



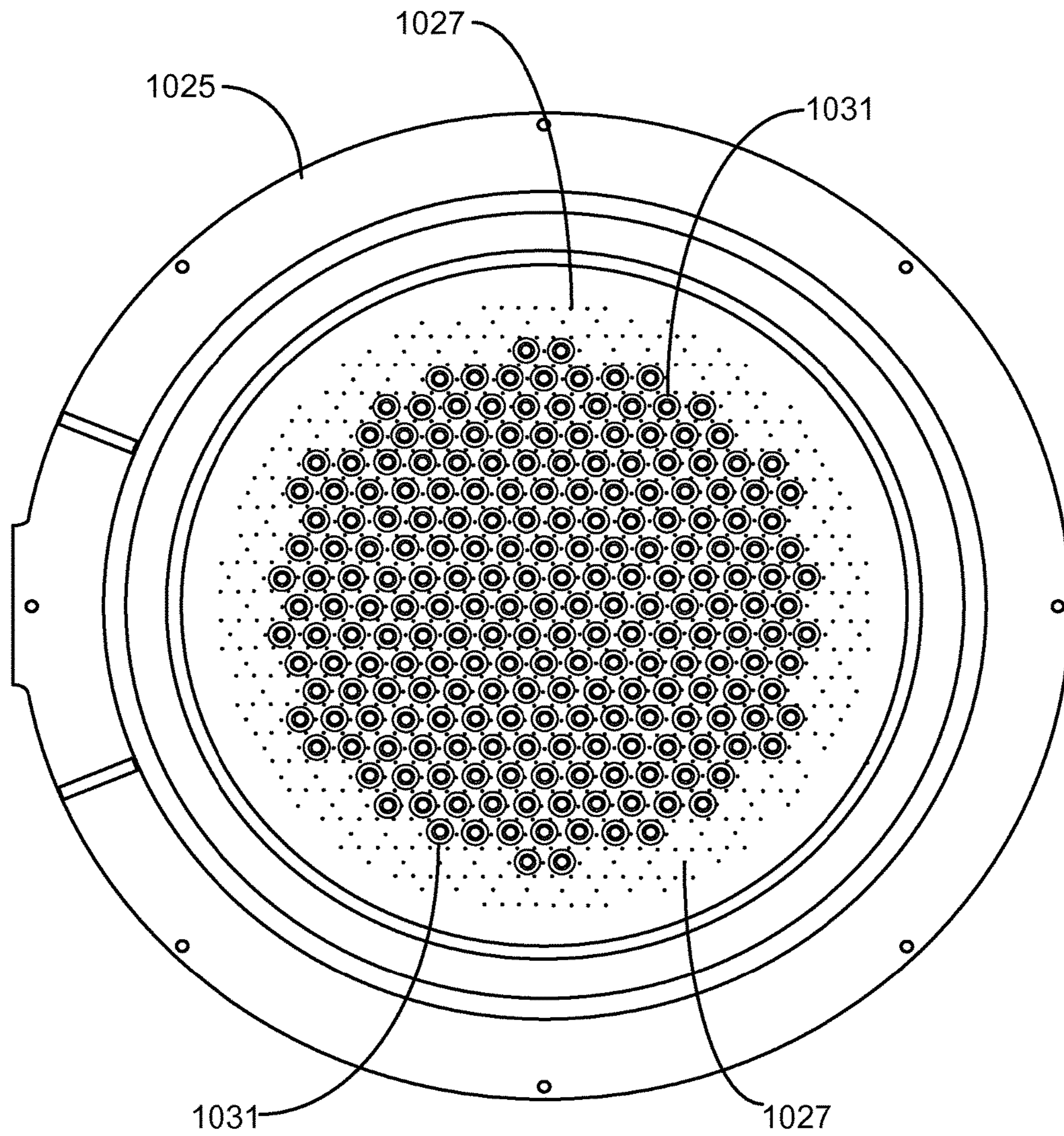


FIG. 3C

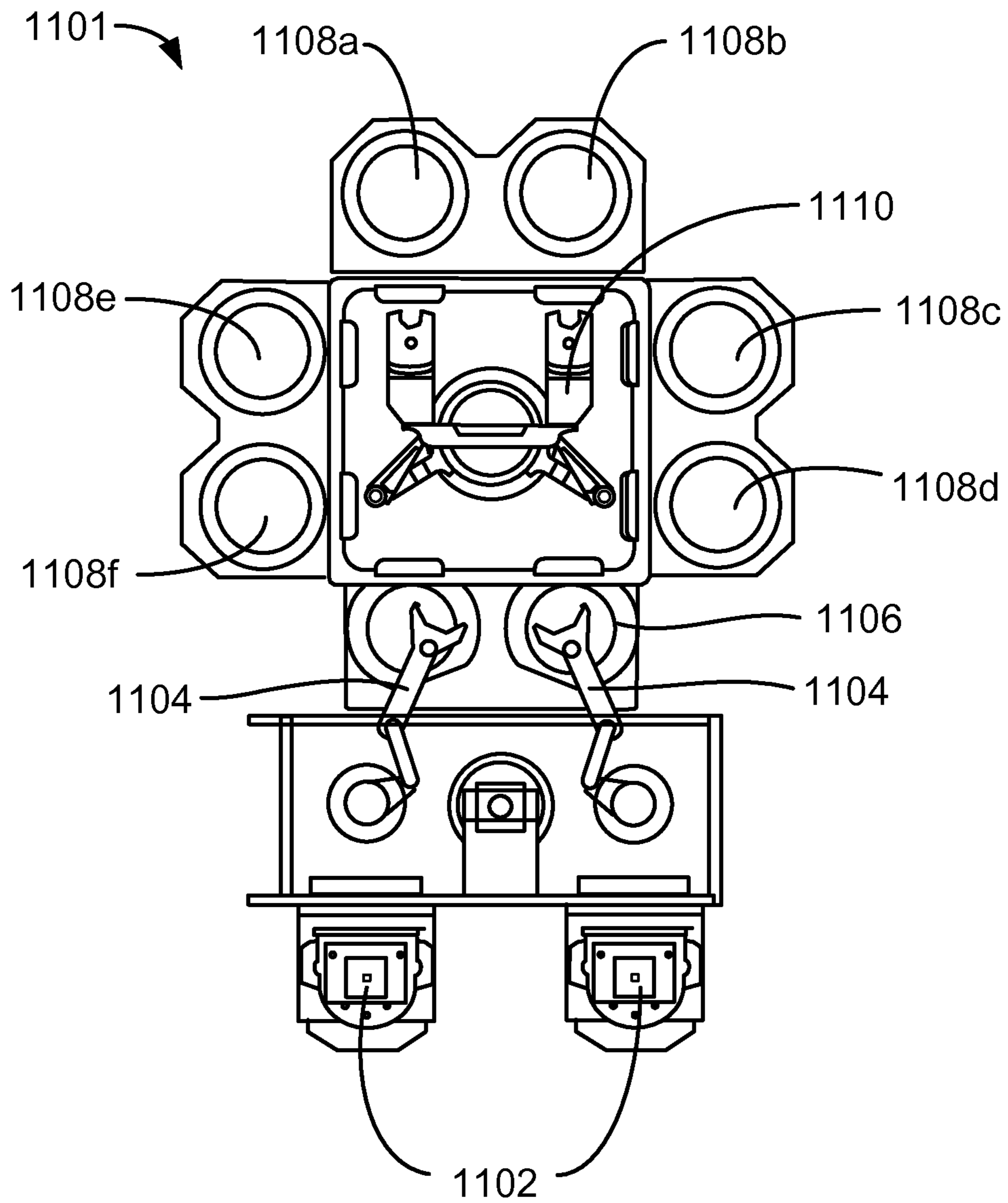


FIG. 4



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## OXIDE ETCH SELECTIVITY ENHANCEMENT

### CROSS-REFERENCES TO RELATED APPLICATIONS

This application claims the benefit of U.S. Prov. Pat. App. No. 62/055,587 filed Sep. 25, 2014, and titled "R3X WITH O2 ADDITION" by Chen et al., which is hereby incorporated herein in its entirety by reference for all purposes.

### FIELD

Embodiments of the invention relate to selectively etching silicon oxide.

### BACKGROUND

Integrated circuits are made possible by processes which produce intricately patterned material layers on substrate surfaces. Producing patterned material on a substrate requires controlled methods for removal of exposed material. Chemical etching is used for a variety of purposes including transferring a pattern in photoresist into underlying layers, thinning layers or thinning lateral dimensions of features already present on the surface. Often it is desirable to have an etch process which etches one material faster than another helping e.g. a pattern transfer process proceed. Such an etch process is said to be selective of the first material relative to the second material. As a result of the diversity of materials, circuits and processes, etch processes have been developed with a selectivity towards a variety of materials.

Dry etch processes are often desirable for selectively removing material from semiconductor substrates. The desirability stems from the ability to gently remove material from miniature structures with minimal physical disturbance. Dry etch processes also allow the etch rate to be abruptly stopped by removing the gas phase reagents. Some dry-etch processes involve the exposure of a substrate to remote plasma by-products formed from one or more precursors. For example, remote plasma excitation of ammonia and nitrogen trifluoride enables silicon oxide to be selectively removed from a patterned substrate when the plasma effluents are flowed into the substrate processing region.

Methods are needed to progressively expand this suite of selectivities in order to enable novel process flows.

### SUMMARY

A method of etching exposed silicon oxide on patterned heterogeneous structures is described and includes a gas phase etch using plasma effluents formed in a remote plasma. The remote plasma excites a fluorine-containing precursor in combination with an oxygen-containing precursor. Plasma effluents within the remote plasma are flowed into a substrate processing region where the plasma effluents combine with water vapor or an alcohol. The combination react with the patterned heterogeneous structures to remove an exposed silicon oxide portion faster than an exposed silicon nitride portion. The inclusion of the oxygen-containing precursor may suppress the silicon nitride etch rate and result in unprecedented silicon oxide etch selectivity.

Embodiments of the invention include methods of etching a patterned substrate. The methods include placing the patterned substrate in a substrate processing region of a substrate processing chamber. The patterned substrate has an exposed silicon oxide portion and an exposed silicon nitride

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portion. The methods further include flowing a radical-fluorine precursor into the substrate processing region. The methods further include flowing a radical-oxygen precursor into the substrate processing region. The methods further include flowing a hydrogen-and-oxygen-containing precursor into the substrate processing region without first passing the hydrogen-and-oxygen-containing precursor through any plasma. The hydrogen-and-oxygen-containing precursor comprises an OH group. The methods further include etching the exposed silicon oxide portion. The exposed silicon oxide portion etches at a first etch rate and the second exposed silicon oxide portion etches at a second etch rate which is lower than the first etch rate.

Embodiments of the invention include methods of etching a patterned substrate. The methods include placing the patterned substrate in a substrate processing region of a substrate processing chamber. The patterned substrate includes an exposed silicon oxide portion and an exposed silicon nitride portion. The methods further include flowing a fluorine-containing precursor and an oxygen-containing precursor into a remote plasma region fluidly coupled to the substrate processing region while forming a remote plasma in the remote plasma region to produce plasma effluents. The methods further include flowing a hydrogen-and-oxygen-containing precursor into the substrate processing region without first passing the hydrogen-and-oxygen-containing precursor through the remote plasma region. The hydrogen-and-oxygen-containing precursor comprises an O—H bond. The methods further include etching the exposed silicon oxide portion by flowing the plasma effluents into the substrate processing region. The exposed silicon oxide portion etches at a first etch rate and the exposed silicon nitride portion etches at a second etch rate which is lower than the first etch rate.

Embodiments of the invention include methods of etching a patterned substrate. The methods include placing the patterned substrate in a substrate processing region of a substrate processing chamber. The patterned substrate has an exposed silicon oxide portion and an exposed silicon nitride portion. The methods further include flowing nitrogen trifluoride and molecular oxygen into a remote plasma region fluidly coupled to the substrate processing region while forming a remote plasma in the remote plasma region to produce plasma effluents. The methods further include combining the plasma effluents with water vapor in the substrate processing region. The methods further include etching the exposed silicon oxide portion with the combination of the plasma effluents and the water vapor. The exposed silicon oxide portion etches at a first etch rate and the exposed silicon nitride portion etches at a second etch rate which is lower than the first etch rate.

Additional embodiments and features are set forth in part in the description that follows, and in part will become apparent to those skilled in the art upon examination of the specification or may be learned by the practice of the disclosed embodiments. The features and advantages of the disclosed embodiments may be realized and attained by means of the instrumentalities, combinations, and methods described in the specification.

### DESCRIPTION OF THE DRAWINGS

A further understanding of the nature and advantages of the embodiments may be realized by reference to the remaining portions of the specification and the drawings.

FIG. 1 is a flow chart of a silicon oxide selective etch process according to embodiments.



FIG. 2 is a plot of silicon nitride etch loss according to embodiments.

FIG. 3A shows a schematic cross-sectional view of a substrate processing chamber according to embodiments.

FIG. 3B shows a schematic cross-sectional view of a portion of a substrate processing chamber according to embodiments.

FIG. 3C shows a bottom view of a showerhead according to embodiments.

FIG. 4 shows a top view of an exemplary substrate processing system according to embodiments.

In the appended figures, similar components and/or features may have the same reference label. Further, various components of the same type may be distinguished by following the reference label by a dash and a second label that distinguishes among the similar components. If only the first reference label is used in the specification, the description is applicable to any one of the similar components having the same first reference label irrespective of the second reference label.

#### DETAILED DESCRIPTION

A method of etching exposed silicon oxide on patterned heterogeneous structures is described and includes a gas phase etch using plasma effluents formed in a remote plasma. The remote plasma excites a fluorine-containing precursor in combination with an oxygen-containing precursor. Plasma effluents within the remote plasma are flowed into a substrate processing region where the plasma effluents combine with water vapor or an alcohol. The combination react with the patterned heterogeneous structures to remove an exposed silicon oxide portion faster than an exposed silicon nitride portion. The inclusion of the oxygen-containing precursor may suppress the silicon nitride etch rate and result in unprecedented silicon oxide etch selectivity.

Selective remote gas phase etch processes have used a hydrogen-containing precursor of ammonia ( $\text{NH}_3$ ) and a fluorine-containing precursor of nitrogen trifluoride ( $\text{NF}_3$ ) which together flow through a remote plasma and into a substrate processing region. Alternative remote gas phase etch processes have also been developed which do not require ammonia. These remote gas phase etch processes remove oxide films much more rapidly than, e.g. silicon. However, even with the alternative processes, there is still a non-negligible loss of silicon nitride which is becoming a problem as linewidths decrease toward and below ten nanometers. The methods disclosed herein may exhibit a significantly greater etch rate selectivity of silicon oxide (regardless of dopants or deposition method) relative to silicon nitride.

In order to better understand and appreciate the invention, reference is now made to FIG. 1 which is a flow chart of a silicon oxide selective etch process **101** according to embodiments. Prior to the first operation, the substrate is patterned and an exposed silicon oxide portion is formed on the patterned substrate. An exposed silicon nitride portion is also formed on the patterned substrate. The patterned substrate is then placed within the substrate processing region in operation **110**.

Nitrogen trifluoride and molecular oxygen ( $\text{O}_2$ ) are flowed into a remote plasma region (operation **120**). The nitrogen trifluoride and oxygen are collectively excited in a remote plasma formed in the remote plasma region. The remote plasma system is positioned next to the substrate processing region and fluidly coupled through a showerhead. The remote plasma region may be within a distinct

module from the processing chamber and/or a compartment within the processing chamber. The plasma effluents formed in the remote plasma are then flowed into the substrate processing region (operation **130**). Water vapor is simultaneously flowed into the substrate processing region and combined with the plasma effluents. The water vapor is not passed through the remote plasma region and therefore may only be excited by interaction with the plasma effluents according to embodiments. The water vapor is not passed through any remote plasma region before entering the substrate processing region in embodiments.

Other sources of fluorine may be used to augment or replace the nitrogen trifluoride. In general, a fluorine-containing precursor is flowed into the plasma region and the fluorine-containing precursor comprises at least one precursor selected from the group consisting of atomic fluorine, diatomic fluorine, nitrogen trifluoride, carbon tetrafluoride, hydrogen fluoride and xenon difluoride in embodiments. Other sources of oxygen may be used to augment or replace the nitrogen trifluoride. In general, an oxygen-containing precursor is flowed into the plasma region and the fluorine-containing precursor comprises at least one precursor selected from the group consisting of molecular oxygen ( $\text{O}_2$ ), ozone ( $\text{O}_3$ ), dinitrogen oxide ( $\text{N}_2\text{O}$ ), hyponitrite ( $\text{N}_2\text{O}_2$ ) or nitrogen dioxide ( $\text{NO}_2$ ) in embodiments.

The patterned substrate is selectively etched (operation **140**) such that the exposed silicon oxide is removed at a higher rate than the exposed silicon nitride. The reactive chemical species are removed and the substrate is removed from the substrate processing region (operation **150**).

Reference is now made to FIG. 2 which is a plot of silicon nitride etch loss during silicon oxide etch processes including etch process **101** according to embodiments. The addition of the oxygen-containing precursor reduces the etch loss of silicon nitride regardless of whether the nitrogen trifluoride is flowed with a high flow rate (**210**), medium flow rate (**220**) or low flow rate (**210**). The low flow rate curve corresponds with a nitrogen trifluoride flow rate of 5 sccm. The medium flow rate and high flow rate curves correspond with 15 sccm and 25 sccm, respectively. At a low  $\text{NF}_3$  flow rate of 5 sccm, the loss of silicon nitride is highest of all three flow rates when no oxygen-containing precursor is included in the remote plasma region. Low  $\text{NF}_3$  flow rates are desirable for many applications to increase selectivity amongst different quality silicon oxide portions. As oxygen-containing precursor is introduced and its flow rate increased, the silicon nitride etch loss plummets in the case of the low nitrogen trifluoride flow rate such that the etch loss even drops below the medium and high flow rates. Combining the low flow rate of nitrogen trifluoride with a moderate flow of oxygen-containing precursor results in an unprecedented silicon oxide etch selectivity relative to silicon nitride.

The methods presented herein exhibit high etch selectivity of the exposed silicon oxide portion relative to an exposed silicon nitride portion. In operation **140**, the etch selectivity of the exposed silicon oxide portion relative to the exposed silicon nitride portion may be greater than 80:1, greater than 120:1 or greater than 150:1 according to embodiments. The etch rate of the exposed silicon oxide portion may be referred to as the first etch rate and the etch rate of the silicon nitride portion may be referred to herein as the second etch rate. The first etch rate may exceed the second etch rate by a factor of more than 80, more than 120 or more than 150 in embodiments. The observed selectivity (silicon oxide relative to silicon nitride) depends on the deposition technique, quality and dopant levels in the silicon oxide. In one



example the selectivity was observed to increase from 130 to 220 using the techniques presented herein for low quality sacrificial silicon oxide. Thus, the first etch rate may exceed the second etch rate by a factor of more than 150, more than 175 or more than 200 in some embodiments.

Cycling has been found to further increase the observed etch selectivities of silicon oxide relative to silicon nitride. Therefore, the unused reactants and other process effluents may be removed from the substrate processing region after operation 140 and before operation 150. Following process effluent removal, operations 120-140 or operations 130-140 may be repeated to remove additional silicon oxide from the exposed silicon oxide portion.

The gas phase etches described herein may not produce solid residue even at low substrate temperatures. Elimination of solid residue during the process avoids any potential disturbance of delicate features such as thin line structures. Elimination of solid residue also simplifies the process flows and decreases processing costs by removing a sublimation step. The fluorine-containing precursor, the remote plasma region and/or the oxygen-containing precursor are devoid of hydrogen during operation 140 in embodiments. The plasma effluents may also be devoid of hydrogen according to embodiments. Lack of hydrogen in the remote plasma region ensures minimal or no production of solid by-products on the patterned substrate.

In the examples presented herein, water was introduced through the showerhead into the substrate processing region without prior plasma excitation. Generally speaking, a hydrogen-and-oxygen-containing precursor may be introduced in place of or to augment the moisture. The hydrogen-and-oxygen-containing precursor may include an OH group in embodiments. The hydrogen-and-oxygen-containing precursor may be one of water or an alcohol according to embodiments. The alcohol may include one or more of methanol, ethanol and isopropyl alcohol in embodiments. The hydrogen-and-oxygen-containing-precursor may not pass through a remote plasma before entering the substrate processing region according to embodiments.

The pressure in the substrate processing region and the remote plasma region(s) during the etching operations may be between 0.1 Torr and 50 Torr, between 1 Torr and 15 Torr or between 5 Torr and 10 Torr in embodiments. The temperature of the patterned substrate during the etching operations may be between  $-20^{\circ}$  C. and  $250^{\circ}$  C., between  $0^{\circ}$  C. and  $50^{\circ}$  C. or between  $5^{\circ}$  C. and  $20^{\circ}$  C. in embodiments. Flow rate ranges are given in the course of describing exemplary equipment.

The method also includes applying power to the fluorine-containing precursor and the oxygen-containing precursor during operation 120 in the remote plasma regions to generate the plasma effluents. The plasma parameters described herein apply to remote plasmas used to etch the patterned substrate. As would be appreciated by one of ordinary skill in the art, the plasma may include a number of charged and neutral species including radicals and ions. The plasma may be generated using known techniques (e.g., RF, capacitively coupled, inductively coupled). In an embodiment, the remote plasma power may be applied to the remote plasma region at a level between 500 W and 10 kW for a remote plasma external to the substrate processing chamber. The remote plasma power may be applied using inductive coils, in embodiments, in which case the remote plasma will be referred to as an inductively-coupled plasma (ICP) or may be applied using capacitive plates, in which case the remote plasma will be referred to as a capacitive-coupled plasma (CCP). According to embodiments, the remote

plasma power may be applied to the remote plasma region at a level between 25 watts and 500 watts for a remote plasma within the substrate processing chamber. Other possible plasma parameters and ranges will be described along with exemplary equipment herein.

For both treatment remote plasmas and etch remote plasmas, the flows of the precursors into the remote plasma region may further include one or more relatively inert gases such as He, N<sub>2</sub>, Ar. The inert gas can be used to improve plasma stability, ease plasma initiation, and improve process uniformity. Argon may be helpful, as an additive, to promote the formation of a stable plasma. Process uniformity is generally increased when helium is included. These additives are present in embodiments throughout this specification. Flow rates and ratios of the different gases may be used to control etch rates and etch selectivity.

In embodiments, an ion suppressor (which may be the showerhead) may be used to provide radical and/or neutral species for gas-phase etching. The ion suppressor may also be referred to as an ion suppression element. In embodiments, for example, the ion suppressor is used to filter etching plasma effluents en route from the remote plasma region to the substrate processing region. The ion suppressor may be used to provide a reactive gas having a higher concentration of radicals than ions. Plasma effluents pass through the ion suppressor disposed between the remote plasma region and the substrate processing region. The ion suppressor functions to dramatically reduce or substantially eliminate ionic species traveling from the plasma generation region to the substrate. The ion suppressors described herein are simply one way to achieve a low electron temperature in the substrate processing region during the gas-phase etch processes described herein.

In embodiments, an electron beam is passed through the substrate processing region in a plane parallel to the substrate to reduce the electron temperature of the plasma effluents. A simpler showerhead may be used if an electron beam is applied in this manner. The electron beam may be passed as a laminar sheet disposed above the substrate in embodiments. The electron beam provides a source of neutralizing negative charge and provides a more active means for reducing the flow of positively charged ions towards the substrate and increasing the etch selectivity in embodiments. The flow of plasma effluents and various parameters governing the operation of the electron beam may be adjusted to lower the electron temperature measured in the substrate processing region.

The electron temperature may be measured using a Langmuir probe in the substrate processing region during excitation of a plasma in the remote plasma. In aluminum removal embodiments, the electron temperature may be less than 0.5 eV, less than 0.45 eV, less than 0.4 eV, or less than 0.35 eV. These extremely low values for the electron temperature are enabled by the presence of the electron beam, showerhead and/or the ion suppressor. Uncharged neutral and radical species may pass through the electron beam and/or the openings in the ion suppressor to react at the substrate. Such a process using radicals and other neutral species can reduce plasma damage compared to conventional plasma etch processes that include sputtering and bombardment. Embodiments of the present invention are also advantageous over conventional wet etch processes where surface tension of liquids can cause bending and peeling of small features. In point of contrast, the electron temperature during the aluminum oxide removal process may be greater than 0.5 eV, greater than 0.6 eV or greater than 0.7 eV according to embodiments.



The substrate processing region may be described herein as “plasma-free” during the etch processes described herein. “Plasma-free” does not necessarily mean the region is devoid of plasma. Ionized species and free electrons created within the plasma region may travel through pores (apertures) in the partition (showerhead) at exceedingly small concentrations. The borders of the plasma in the chamber plasma region may encroach to some small degree upon the substrate processing region through the apertures in the showerhead. Furthermore, a low intensity plasma may be created in the substrate processing region without eliminating desirable features of the etch processes described herein. All causes for a plasma having much lower intensity ion density than the chamber plasma region during the creation of the excited plasma effluents do not deviate from the scope of “plasma-free” as used herein.

FIG. 3A shows a cross-sectional view of an exemplary substrate processing chamber **1001** with a partitioned plasma generation region within the processing chamber. During film etching, a process gas may be flowed into chamber plasma region **1015** through a gas inlet assembly **1005**. A remote plasma system (RPS) **1002** may optionally be included in the system, and may process a first gas which then travels through gas inlet assembly **1005**. The process gas may be excited within RPS **1002** prior to entering chamber plasma region **1015**. Accordingly, the fluorine-containing precursor as discussed above, for example, may pass through RPS **1002** or bypass the RPS unit in embodiments.

A cooling plate **1003**, faceplate **1017**, ion suppressor **1023**, showerhead **1025**, and a substrate support **1065** (also known as a pedestal), having a substrate **1055** disposed thereon, are shown and may each be included according to embodiments. Pedestal **1065** may have a heat exchange channel through which a heat exchange fluid flows to control the temperature of the substrate. This configuration may allow the substrate **1055** temperature to be cooled or heated to maintain relatively low temperatures, such as between  $-20^{\circ}$  C. to  $200^{\circ}$  C. Pedestal **1065** may also be resistively heated to relatively high temperatures, such as between  $100^{\circ}$  C. and  $1100^{\circ}$  C., using an embedded heater element.

Exemplary configurations may include having the gas inlet assembly **1005** open into a gas supply region **1058** partitioned from the chamber plasma region **1015** by faceplate **1017** so that the gases/species flow through the holes in the faceplate **1017** into the chamber plasma region **1015**. Structural and operational features may be selected to prevent significant backflow of plasma from the chamber plasma region **1015** back into the supply region **1058**, gas inlet assembly **1005**, and fluid supply system **1010**. The structural features may include the selection of dimensions and cross-sectional geometries of the apertures in faceplate **1017** to deactivate back-streaming plasma. The operational features may include maintaining a pressure difference between the gas supply region **1058** and chamber plasma region **1015** that maintains a unidirectional flow of plasma through the showerhead **1025**. The faceplate **1017**, or a conductive top portion of the chamber, and showerhead **1025** are shown with an insulating ring **1020** located between the features, which allows an AC potential to be applied to the faceplate **1017** relative to showerhead **1025** and/or ion suppressor **1023**. The insulating ring **1020** may be positioned between the faceplate **1017** and the showerhead **1025** and/or ion suppressor **1023** enabling a capacitively coupled plasma (CCP) to be formed in the chamber plasma region.

The plurality of holes in the ion suppressor **1023** may be configured to control the passage of the activated gas, i.e., the ionic, radical, and/or neutral species, through the ion suppressor **1023**. For example, the aspect ratio of the holes, or the hole diameter to length, and/or the geometry of the holes may be controlled so that the flow of ionically-charged species in the activated gas passing through the ion suppressor **1023** is reduced. The holes in the ion suppressor **1023** may include a tapered portion that faces chamber plasma region **1015**, and a cylindrical portion that faces the showerhead **1025**. The cylindrical portion may be shaped and dimensioned to control the flow of ionic species passing to the showerhead **1025**. An adjustable electrical bias may also be applied to the ion suppressor **1023** as an additional means to control the flow of ionic species through the suppressor. The ion suppression element **1023** may function to reduce or eliminate the amount of ionically charged species traveling from the plasma generation region to the substrate. Uncharged neutral and radical species may still pass through the openings in the ion suppressor to react with the substrate.

Plasma power can be of a variety of frequencies or a combination of multiple frequencies. In the exemplary processing system the plasma may be provided by RF power delivered to faceplate **1017** relative to ion suppressor **1023** and/or showerhead **1025**. The RF power may be between about 10 watts and about 5000 watts, between about 100 watts and about 2000 watts, between about 200 watts and about 1500 watts, or between about 200 watts and about 1000 watts in embodiments. The RF frequency applied in the exemplary processing system may be low RF frequencies less than about 200 kHz, high RF frequencies between about 10 MHz and about 15 MHz, or microwave frequencies greater than or about 1 GHz in embodiments. The plasma power may be capacitively-coupled (CCP) or inductively-coupled (ICP) into the remote plasma region.

A precursor, for example a fluorine-containing precursor and an oxygen-containing precursor, may be flowed into substrate processing region **1033** by embodiments of the showerhead described herein. Excited species derived from the process gas in chamber plasma region **1015** may travel through apertures in the ion suppressor **1023**, and/or showerhead **1025** and react with an additional precursor flowing into substrate processing region **1033** from a separate portion of the showerhead. Alternatively, if all precursor species are being excited in chamber plasma region **1015**, no additional precursors may be flowed through the separate portion of the showerhead. Little or no plasma may be present in substrate processing region **1033** during the remote plasma etch process. Excited derivatives of the precursors may combine in the region above the substrate and/or on the substrate to etch structures or remove species from the substrate.

The processing gases may be excited in chamber plasma region **1015** and may be passed through the showerhead **1025** to substrate processing region **1033** in the excited state. While a plasma may be generated in substrate processing region **1033**, a plasma may alternatively not be generated in the processing region. In one example, the only excitation of the processing gas or precursors may be from exciting the processing gases in chamber plasma region **1015** to react with one another in substrate processing region **1033**. As previously discussed, this may be to protect the structures patterned on substrate **1055**.

FIG. 3B shows a detailed view of the features affecting the processing gas distribution through faceplate **1017**. The gas distribution assemblies such as showerhead **1025** for use



in the processing chamber section **1001** may be referred to as dual channel showerheads (DCSH) and are additionally detailed in the embodiments described in FIG. 3A as well as FIG. 3C herein. The dual channel showerhead may provide for etching processes that allow for separation of etchants outside of the processing region **1033** to provide limited interaction with chamber components and each other prior to being delivered into the processing region.

The showerhead **1025** may comprise an upper plate **1014** and a lower plate **1016**. The plates may be coupled with one another to define a volume **1018** between the plates. The coupling of the plates may be so as to provide first fluid channels **1019** through the upper and lower plates, and second fluid channels **1021** through the lower plate **1016**. The formed channels may be configured to provide fluid access from the volume **1018** through the lower plate **1016** via second fluid channels **1021** alone, and the first fluid channels **1019** may be fluidly isolated from the volume **1018** between the plates and the second fluid channels **1021**. The volume **1018** may be fluidly accessible through a side of the gas distribution assembly **1025**. Although the exemplary system of FIGS. 3A-3C includes a dual-channel showerhead, it is understood that alternative distribution assemblies may be utilized that maintain first and second precursors fluidly isolated prior to substrate processing region **1033**. For example, a perforated plate and tubes underneath the plate may be utilized, although other configurations may operate with reduced efficiency or not provide as uniform processing as the dual-channel showerhead described.

In the embodiment shown, showerhead **1025** may distribute via first fluid channels **1019** process gases which contain plasma effluents upon excitation by a plasma in chamber plasma region **1015**. In embodiments, the process gas introduced into RPS **1002** and/or chamber plasma region **1015** may contain fluorine, e.g.,  $\text{NF}_3$ . The process gas may also include a carrier gas such as helium, argon, nitrogen ( $\text{N}_2$ ), etc. Plasma effluents may include ionized or neutral derivatives of the process gas and may also be referred to herein as a radical-fluorine precursor referring to the atomic constituent of the process gas introduced.

FIG. 3C is a bottom view of a showerhead **1025** for use with a processing chamber in embodiments. Showerhead **1025** corresponds with the showerhead shown in FIG. 3A. Through-holes **1031**, which show a view of first fluid channels **1019**, may have a plurality of shapes and configurations to control and affect the flow of precursors through the showerhead **1025**. Small holes **1027**, which show a view of second fluid channels **1021**, may be distributed substantially evenly over the surface of the showerhead, even amongst the through-holes **1031**, which may help to provide more even mixing of the precursors as they exit the showerhead than other configurations.

The chamber plasma region **1015** or a region in an RPS may be referred to as a remote plasma region. In embodiments, the radical-fluorine precursor and the radical-oxygen precursor are created in the remote plasma region and travel into the substrate processing region to combine with the hydrogen-and-oxygen-containing precursor. In embodiments, the hydrogen-and-oxygen-containing precursor is excited only by the radical-fluorine precursor and the radical-oxygen precursor. Plasma power may essentially be applied only to the remote plasma region in embodiments to ensure that the radical-fluorine precursor and the radical-oxygen precursor provide the dominant excitation.

Embodiments of the dry etch systems may be incorporated into larger fabrication systems for producing integrated circuit chips. FIG. 4 shows one such processing system

(mainframe) **1101** of deposition, etching, baking, and curing chambers in embodiments. In the figure, a pair of front opening unified pods (load lock chambers **1102**) supply substrates of a variety of sizes that are received by robotic arms **1104** and placed into a low pressure holding area **1106** before being placed into one of the substrate processing chambers **1108a-f**. A second robotic arm **1110** may be used to transport the substrate wafers from the holding area **1106** to the substrate processing chambers **1108a-f** and back. Each substrate processing chamber **1108a-f**, can be outfitted to perform a number of substrate processing operations including the dry etch processes described herein in addition to cyclical layer deposition (CLD), atomic layer deposition (ALD), chemical vapor deposition (CVD), physical vapor deposition (PVD), etch, pre-clean, degas, orientation, and other substrate processes.

Nitrogen trifluoride (or another fluorine-containing precursor) may be flowed into chamber plasma region **1020** at rates between about 1 sccm and about 40 sccm, between about 3 sccm and about 25 sccm or between about 5 sccm and about 10 sccm in embodiments. Oxygen (or another oxygen-containing precursor) may be flowed into chamber plasma region **1020** at rates between about 10 sccm and about 400 sccm, between about 30 sccm and about 250 sccm or between about 50 sccm and about 150 sccm in embodiments. Water vapor may be flowed into substrate processing region **1070** at rates between about 5 sccm and about 100 sccm, between about 10 sccm and about 50 sccm or between about 15 sccm and about 25 sccm according to embodiments. The flow rate ratio of the oxygen-containing precursor to the fluorine-containing precursor may be greater than 4, greater than 6 or greater than 10 according to embodiments. The flow rate ratio of the oxygen-containing precursor to the fluorine-containing precursor may be less than 40, less than 30 or less than 20 in embodiments. Upper limits may be combined with lower limits according to embodiments.

The showerhead may be referred to as a dual-channel showerhead as a result of the two distinct pathways into the substrate processing region. The fluorine-containing precursor and the oxygen-containing precursor may be flowed through the through-holes in the dual-zone showerhead and the water vapor may pass through separate zones in the dual-zone showerhead. The separate zones may open into the substrate processing region but not into the remote plasma region as described above.

Combined flow rates of water vapor and plasma effluents into the substrate processing region may account for 0.05% to about 20% by volume of the overall gas mixture; the remainder being carrier gases. The fluorine-containing precursor and the oxygen-containing precursor flowed into the remote plasma region but the plasma effluents has the same volumetric flow ratio, in embodiments. In the case of the fluorine-containing precursor, a purge or carrier gas may be first initiated into the remote plasma region before those of the fluorine-containing gas and the oxygen-containing precursor to stabilize the pressure within the remote plasma region.

As used herein "substrate" may be a support substrate with or without layers formed thereon. The patterned substrate may be an insulator or a semiconductor of a variety of doping concentrations and profiles and may, for example, be a semiconductor substrate of the type used in the manufacture of integrated circuits. Exposed "silicon oxide" of the patterned substrate is predominantly  $\text{SiO}_2$  but may include concentrations of other elemental constituents such as, e.g., nitrogen, hydrogen and carbon. In some embodiments, sili-



con oxide portions etched using the methods disclosed herein consist essentially of silicon and oxygen. Exposed “silicon nitride” of the patterned substrate is predominantly  $\text{Si}_3\text{N}_4$  but may include concentrations of other elemental constituents such as, e.g., oxygen, hydrogen and carbon. In some embodiments, silicon nitride portions described herein consist essentially of silicon and nitrogen.

The terms “gap” and “trench” are used throughout with no implication that the etched geometry has a large horizontal aspect ratio. Viewed from above the surface, trenches may appear circular, oval, polygonal, rectangular, or a variety of other shapes. A trench may be in the shape of a moat around an island of material. The term “via” is used to refer to a low aspect ratio trench (as viewed from above) which may or may not be filled with metal to form a vertical electrical connection. As used herein, a conformal etch process refers to a generally uniform removal of material on a surface in the same shape as the surface, i.e., the surface of the etched layer and the pre-etch surface are generally parallel. A person having ordinary skill in the art will recognize that the etched interface likely cannot be 100% conformal and thus the term “generally” allows for acceptable tolerances.

The term “precursor” is used to refer to any process gas which takes part in a reaction to either remove material from or deposit material onto a surface. “Plasma effluents” describe gas exiting from the chamber plasma region and entering the substrate processing region. Plasma effluents are in an “excited state” wherein at least some of the gas molecules are in vibrationally-excited, dissociated and/or ionized states. A “radical precursor” is used to describe plasma effluents (a gas in an excited state which is exiting a plasma) which participate in a reaction to either remove material from or deposit material on a surface. “Radical-fluorine precursors” describe radical precursors which contain fluorine but may contain other elemental constituents. “Radical-oxygen precursors” describe radical precursors which contain oxygen but may contain other elemental constituents. The phrase “inert gas” refers to any gas which does not form chemical bonds when etching or being incorporated into a film. Exemplary inert gases include noble gases but may include other gases so long as no chemical bonds are formed when (typically) trace amounts are trapped in a film.

Having disclosed several embodiments, it will be recognized by those of skill in the art that various modifications, alternative constructions, and equivalents may be used without departing from the spirit of the disclosed embodiments. Additionally, a number of well-known processes and elements have not been described in order to avoid unnecessarily obscuring the present invention. Accordingly, the above description should not be taken as limiting the scope of the invention.

Where a range of values is provided, it is understood that each intervening value, to the tenth of the unit of the lower limit unless the context clearly dictates otherwise, between the upper and lower limits of that range is also specifically disclosed. Each smaller range between any stated value or intervening value in a stated range and any other stated or intervening value in that stated range is encompassed. The upper and lower limits of these smaller ranges may independently be included or excluded in the range, and each range where either, neither or both limits are included in the smaller ranges is also encompassed within the invention, subject to any specifically excluded limit in the stated range. Where the stated range includes one or both of the limits, ranges excluding either or both of those included limits are also included.

As used herein and in the appended claims, the singular forms “a”, “an”, and “the” include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to “a process” includes a plurality of such processes and reference to “the dielectric material” includes reference to one or more dielectric materials and equivalents thereof known to those skilled in the art, and so forth.

Also, the words “comprise,” “comprising,” “include,” “including,” and “includes” when used in this specification and in the following claims are intended to specify the presence of stated features, integers, components, or steps, but they do not preclude the presence or addition of one or more other features, integers, components, steps, acts, or groups.

The invention claimed is:

1. A method of etching a patterned substrate, the method comprising:

placing the patterned substrate in a substrate processing region of a substrate processing chamber, wherein the patterned substrate comprises an exposed silicon oxide portion and an exposed silicon nitride portion;

flowing a fluorine-containing precursor and an oxygen-containing precursor into a remote plasma region fluidly coupled to the substrate processing region while forming a remote plasma in the remote plasma region to produce plasma effluents;

flowing a hydrogen-and-oxygen-containing precursor into the substrate processing region without first passing the hydrogen-and-oxygen-containing precursor through the remote plasma region, wherein the hydrogen-and-oxygen-containing precursor comprises an O—H bond; and

etching the exposed silicon oxide portion by flowing the plasma effluents into the substrate processing region, wherein the exposed silicon oxide portion etches at a first etch rate and the exposed silicon nitride portion etches at a second etch rate which is lower than the first etch rate.

2. The method of claim 1 wherein the first etch rate exceeds the second etch rate by a factor of about 80 or more.

3. The method of claim 1 wherein the substrate processing region is plasma-free during the operation of etching the exposed silicon oxide portion.

4. The method of claim 1 wherein the hydrogen-and-oxygen-containing precursor is not excited by any plasma outside the substrate processing region prior to entering the substrate processing region.

5. The method of claim 1 wherein the fluorine-containing precursor comprises a precursor selected from the group consisting of atomic fluorine, diatomic fluorine, nitrogen trifluoride, carbon tetrafluoride, hydrogen fluoride and xenon difluoride.

6. The method of claim 1 wherein the remote plasma region, the substrate processing region, the fluorine-containing precursor, the oxygen-containing precursor and the plasma effluents are essentially devoid of hydrogen during the operation of etching the exposed silicon oxide portion.

7. The method of claim 1 wherein the fluorine-containing precursor and the oxygen-containing precursor flow through through-holes in a dual-zone showerhead and the hydrogen-and-oxygen-containing precursor passes through separate zones in the dual-zone showerhead, wherein the separate zones open into the substrate processing region but not directly into the remote plasma region.

8. The method of claim 1 wherein the hydrogen-and-oxygen-containing precursor comprises one of water vapor or an alcohol.



9. The method of claim 1 wherein the oxygen-containing precursor comprises one or more of O<sub>2</sub>, O<sub>3</sub>, N<sub>2</sub>O, NO<sub>2</sub> and N<sub>2</sub>O<sub>2</sub>.

10. A method of etching a patterned substrate, the method comprising:

placing the patterned substrate in a substrate processing region of a substrate processing chamber, wherein the patterned substrate comprises an exposed silicon oxide portion and an exposed silicon nitride portion;

flowing nitrogen trifluoride and molecular oxygen into a remote plasma region fluidly coupled to the substrate processing region while forming a remote plasma in the remote plasma region to produce plasma effluents;

combining the plasma effluents with water vapor in the substrate processing region; and

etching the exposed silicon oxide portion with the combination of the plasma effluents and the water vapor, wherein the exposed silicon oxide portion etches at a first etch rate and the exposed silicon nitride portion etches at a second etch rate which is lower than the first etch rate.

11. The method of claim 10 wherein the water vapor is flowed into the remote plasma region without first passing through the remote plasma region.

12. The method of claim 10 wherein the first etch rate exceeds the second etch rate by a factor of about 120 or more.

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